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REPORT

hiRX performance testing at SRNL using spent nuclear fuel

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Abstract

Testing of the alpha-prototype high-resolution X-ray spectrometer (hiRX) instrument at Savannah River National Laboratory (SRNL) has demonstrated significant potential for using the hiRX instrument for Pu measurements in safeguards applications as well as other actinide processing systems. This report highlights the good performance of the alpha-prototype hiRX instrument, keeping in mind this is the first-of-a-kind near production hiRX tested on spent nuclear fuel samples. The potential of this alpha-prototype can only be realized with further development and upgrading of both the spectrometer hardware and the manufacturer's instrument control and data reduction software. Achieving an expanded uncertainty for hiRX of less than 1% will require a dedicated effort in identifying and reducing sources of uncertainty within the next several years.

The testing of the instrument performance for both calibration and measurements of spent nuclear fuel and plutonium process samples was a success, exceeding our expectations. The mean results had biases of -0.5 to +3% for Pu and -5% for U in the real samples versus SRNL routine Pu and U accountability methods. The initial results we obtained were satisfactory in that the calibrations for the two suites of solutions: Pu-only in dilute nitric acid (aqueous matrix) and Pu/U in dilute nitric acid (U matrix) gave R^2 values for linear fits of the measured Pu standards of 0.9981 and 0.9880 respectively. The U calibration R^2 value was 0.9778. Several the standards were measured as unknowns giving biases of -18% to -6% for Pu and -18% to +3% for U with relative standard deviation (RSD) values in the range of <1-8%, however these results were obtained before the FP model was corrected. Further refinements of the modeling software are expected to significantly reduce the uncertainty of the Pu and U measurements. Improvements in both software and hardware have been identified to reduce the measurement uncertainties in the hiRX Pu and U results. In the near-term, it appears that upgrading the software will have a greater impact on measurement uncertainty and ease of operations for the alpha-prototype hiRX spectrometer. Hardware upgrades will aid in empirically correcting U matrix effects on both the Pu and U quantification. Modifications to the sample cell filling procedure will also reduce error in the measurements.

The demonstrated simplicity of the hiRX measurement process has highlighted potential applications within Savannah River Site (SRS). The ability to measure a wide range of Pu and U concentration, rapidly, without significant sample preparation or purification and with reduced waste volumes provides a strategic advantage in actinide measurements for materials control and accountability (MC&A), process control, criticality prevention, and waste characterization to name a few potential application areas.

Section 1. Introduction

The hiRX instrument grew out of Los Alamos National Laboratory's (LANL) interest to provide more accurate Pu measurements for safeguards accountancy of the input dissolver tank in a reprocessing plant environment. LANL engaged XOS (X-ray Optical Systems) on conceptual design. LANL applied to NA-241 for funding to design and fabricate the alpha-prototype hiRX and to test it in the SRNL H-Canyon Test Bed. LANL, SRNL, and XOS collaborated on design requirements and features.

While there are existing methods used to measure Pu and U for accountancy, briefly described below, they each have time consuming sample preparation methodologies. The hiRX measurement procedure simply requires placing a small volume of the sample into a sample cell (microcell, 7 μ L capacity) and inserting the microcell into the instrument. The advantage of such simple sample handling combined with the potential of achieving 0.1% uncertainty can provide significantly improved diversion detection [1, 2] as well as addressing the needs of the safeguards community by providing a rapid means for U and Pu measurements. An alpha-prototype hiRX spectrometer has been tested using Pu and U process samples taken from Savannah River Site's (SRS) H-Canyon and HB-Line Nuclear Facilities and Pu and U reference materials prepared by SRNL. This instrument has followed a progression of conceptual testing [3, 4], bread board development [5-7], and prototype design, building and laboratory testing [8-9], resulting in the alpha-prototype instrument test results reported here.

The dissolver tanks in a reprocessing facility contain process solutions that are complex and radiologically and chemically hazardous. The elemental composition of a spent nuclear fuel typically has impurities and fission products from a large part of the Periodic Table. Process samples have high concentrations of uranium, which can provide challenges to many analytical methods. There are a number of methods used to measure U and Pu in spent nuclear fuel samples.

Kinetic Phosphorescence Analysis (KPA) – this method uses a pulsed diode laser to measure low levels of uranium for process solutions and waste stream transfers. The uranium levels are typically 1×10^{-4} to 1×10^1 g/L with $\pm 20\%$ uncertainty. This method involves significant sample preparation prior to making the final measurement. Details on KPA appear in reference [10].

Absorption Spectrophotometry – this method uses UV/Vis spectrophotometers with diode array detectors that measure Pu at the 0.02 to 1.56 g/L levels with $\pm 3.4\%$ uncertainty. The Pu must be reduced to the +3 oxidation state and therefore it is diluted with ferrous sulfamate to ensure the Pu can be measured. Sample preparation is required. See reference [11] for details on the spectrophotometry method.

Alpha Spectrometry – this method uses TEVA™ resin to purify the Pu sample solution. An aliquot of the purified Pu containing an alpha activity of 16-1600 Bq/mL (1×10^3 - 1×10^5 dpm/mL) is deposited onto a planchet. The alpha activity is measured with an expanded uncertainty of 5-10% (coverage factor, K=2; confidence interval of 95%). This method is used at the SRS for process control, nuclear safety, and nuclear material accountability. See reference [12] for background on the use of TEVA™ resins.

Davies & Gray Potentiometric Titration - this method determines the uranium concentration by potentiometric titration of uranium (IV) with a standard solution of potassium dichromate as an oxidizing agent. The preferred range for this method is 20-50 mg U. The sample is pre-treated with a combination of acids, reducing agents, and reduction/oxidation catalysts to reduce all of

the U to U⁴⁺ state. The method is used for concentrations of U 10 to 400 g/L with an expanded uncertainty of $\pm 0.3\%$ (K=2). This method is used at the SRS for process control and nuclear material accountability [13].

Pu and U TIMS/IDMS – sample preparation involves spiking samples with ²⁴⁴Pu and ²³³U tracers followed by column separation to remove interferences. The sample is plated onto a rhenium filament and measured on a thermal ionization mass spectrometer. This measurement covers a range from 0.1-100 g/L for U and 0.1-60 g/L for Pu with expanded uncertainties of $\pm 0.1\%$ (K=2) for major Pu and U isotope ratios and ± 1.5 -2% (K=2) for Pu and U concentration. Samples require significant dilution to get the concentration into an acceptable range for the mass spectrometer. This method is used at the SRS for process control, nuclear safety, and nuclear material accountability [14].

Pu Coulometry – this method utilizes an electrochemical reaction of Pu in sulfuric acid. The concentration range is 0.5-60 g/L with an expanded uncertainty of ± 0.1 -0.2% (K=2). This method is used at the SRS for characterization of working reference materials and nuclear material accountability [15].

Hybrid K-edge (HKED) – this method provides a direct measurement of the sample solution without pretreatment. The transmission of X-rays through a sample solution is measured at two energies that bracket the absorption edge of the element of interest. The method requires 2-5 mL sample solution in a 2-cm path length cell. The concentration range for both U and Pu covers the typical spent fuel concentrations of 150-250 g/L U and 1-3 g/L Pu with uncertainties of 0.2% for U and 0.75% for Pu [16]. A comparison of the major differences between hiRX and HKED is presented in reference [17]. [Note: Hybrid K-edge is not used at the SRS].

In each case, except for hiRX and HKED, there is sample preparation required, and for most laboratory methods the preparations are involved and time consuming, prior to the actual measurement of the analyte, which can also be complex and/or time consuming. This is in contrast with the hiRX methodology of pipetting 7 microliters directly into the microcell, placing the microcell in the sample holder and then inserting it into the instrument. This method provides direct measurement of spent nuclear fuel Pu concentration within 10 minutes of sample introduction.

The existing hiRX technology provides Pu and U measurements that are rapid and easy to perform in a laboratory environment and cover a wide range of concentrations. With continued development and refinement of both software and hardware, this technology can offer lower measurement uncertainties for a wide range of Pu and U applications within the safeguards and nuclear fuel reprocessing arenas.

Section 2. Instrument description and technique

hiRX technology

High resolution X-ray (hiRX) is a new methodology for the direct measurement of Pu and U in spent nuclear fuel. hiRX is a nondestructive elemental analysis technique based on monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) spectrometry [18] that was designed specifically for detection of actinide elements. The basis of MWDXRF is the use of doubly curved crystal (DCC) optics [19] for both excitation and detection. Coupled with an X-ray tube, the point-focusing excitation optic creates a monochromatic source to excite characteristic X-ray fluorescence from the sample, while the collection optic only passes X-rays of specific energies and focuses them on the detector. This provides hiRX with novel elemental sensitivity

and selectivity. Background counts due to X-ray scattering and peaks outside the collection energy are removed from detection. The hiRX alpha-prototype is a fixed-geometry, dual-channel, compact benchtop instrument that is designed for routine analyses of spent nuclear fuel samples. The instrument is solid state with no moving parts and is simple to operate. Minimal sample preparation is required and results are acquired within minutes. Waste disposal and keeping exposure ALARA (As Low As Reasonably Achievable) are important considerations when analyzing radiological materials but using hiRX these concerns are significantly reduced.

hiRX description and operating principles

The hiRX production alpha-prototype was designed and built by X-Ray Optical Systems ((XOS), East Greenbush, NY). It consists of a compact X-ray tube with a rhodium (Rh) anode which can operate at a maximum of 50 kV and 1 mA (50 W). A DCC optic on the X-ray tube provides monochromatic excitation using the Rh $K\alpha$ line at 20.2 keV. The excitation beam spot size is approximately 2.2 mm in diameter focused into the sample cell. The collection optic contains three DCC segments (270°) for Pu X-ray fluorescence at 14.3 keV and one DCC (90°) for U at 13.6 keV. The characteristic X-rays from the sample are focused onto a silicon drift detector (SDD). The instrument exterior is constructed of stainless steel and has dimensions of 30 cm high by 42 cm wide by 59 cm deep. The hiRX alpha-prototype has only one button for instrument power and a door to access the sample chamber. The instrument operates on standard power (110-240 VAC) and weighs 52 kg. The hiRX safety features include an X-ray “ON” indicator light, an interlocking chamber door, and an X-ray tube shutter. The hiRX alpha-prototype is shown in Figure 1. All hiRX measurements at LANL were under 50 kV, 0.8 mA (40W) conditions while measurements at SRNL were at 50 kV, 0.7 mA (35 W).

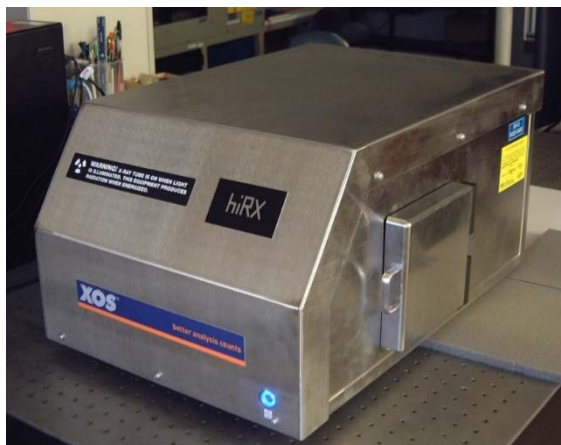


Figure 1. Image of hiRX alpha-prototype instrument at LANL

The hiRX has a user-friendly graphical user interface (GUI) through which all instrument operations are controlled using a standalone PC and monitor. The operator can enter sample information and desired parameters, initiate the measurement process, monitor progress and instrument conditions, and view results using the GUI. General user selectable parameters include measurement time (100, 500, 1000, or 10000 s), calibration type, and reported elements and units (mg/kg (parts-per-million (ppm) by weight) or g/L). Figure 2 is an image of the GUI displaying sample results including a spectrum. hiRX data are saved as tamper-evident “.hdx” files with unique identifiers and can also be exported in “.csv” format. Calibration is performed with a guided series of prompts within the GUI. In addition, the hiRX alpha-prototype includes a leak detection function which notifies the operator of a rapid decrease in signal intensity during sample measurement.

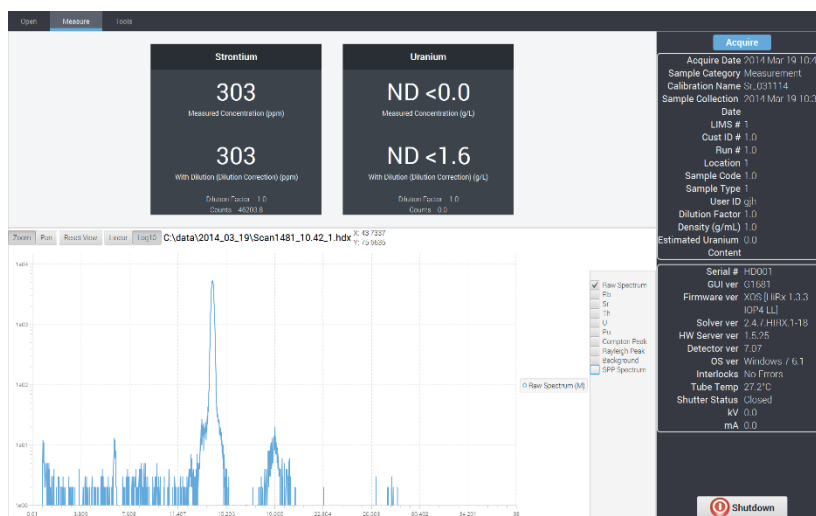


Figure 2. Screenshot of the hiRX GUI showing results for a strontium (Sr) sample

Accurate quantification of Pu and U with hiRX requires calibration of the instrument using traceable Pu and U reference material solutions. In order to produce a calibration curve, the operator measures a minimum of three and a maximum of eight standards. Each standard is measured once for a selected time, which for this evaluation was 100 s for all of the calibrations. Custom calibrations should be completed for each unique type of sample matrix. However, these calibrations can then be utilized over an extended period of time. It is not necessary to generate new calibrations on each analysis day. Recalibration should be completed periodically or when operating conditions change. Day-to-day performance should be monitored with a quality control (QC) standard. Calibrations for two types of matrix were completed on the hiRX alpha-prototype: Pu in aqueous matrix ($\text{HNO}_3/\text{H}_2\text{O}$) and Pu in U-rich matrix ($\text{U}/\text{HNO}_3/\text{H}_2\text{O}$). It should be noted the calibration for the U rich matrix was limited to 100 g/L to accommodate the software model limitations at this point. Future efforts will improve the software model and hardware upgrades will allow calibration over the full range of U matrix concentration. Figure 3 is a simplified block diagram depicting hiRX data processing. hiRX quantification is based on Fundamental Parameters (FP) analysis, a well-established approach in which fundamental constants and known experimental parameters are used to calculate results without operator calibration of instrument response. A component of the system's software referred to as the "Solver" performs the following functions:

- 1) generation of a Spectrum Pre-Processor (SPP) intensity for each element of interest from raw spectral data by summing the counts within a region-of-interest for the major analyte line after background subtraction and peak deconvolution
- 2) conversion of the SPP intensity into a concentration-based FP result
- 3) application of a correction factor on the FP result based on custom calibration, generating CustCal results

The Solver calculation of CustCal results relies upon the use of a linear fitting of the custom calibration curve. Further discussion of the treatment of hiRX data including an evaluation of offline processing appear in Sections 3 and 4.

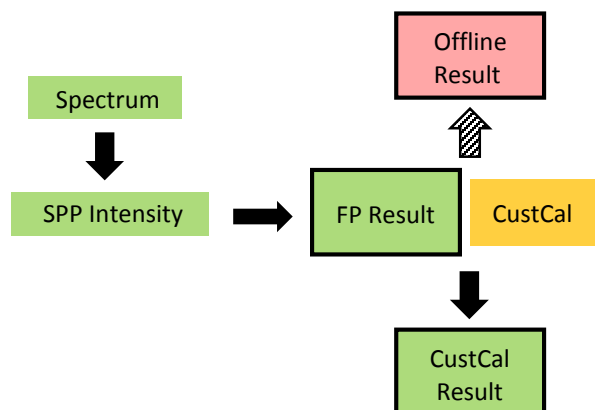


Figure 3. Block diagram showing hiRX data processing. Green boxes are steps handled by hiRX Solver software. Yellow box is the CustCal correction factor, specific to each element and matrix. Outlined boxes are data processing endpoints. SPP Intensity units are counts and Result units are ppm.

Section 3. Experimental

A. Evaluation at Los Alamos National Laboratory

The hiRX alpha-prototype was installed at LANL for laboratory evaluation and method development from February to June 2014. The primary goals were to develop a suitable sample preparation methodology, demonstrate instrument calibration, assess accuracy and precision, and test preliminary performance for Pu and U detection.

Sample handling

A disposable polycarbonate microcell was designed for the hiRX alpha-prototype. The microcell is filled by pipetting 7 μL of sample directly into a chamber in the center of the device. No other sample preparation or pretreatment is required. A small backing disk is placed over the filled chamber. The sample chamber is surrounded by an O-ring to ensure a leak-tight seal, and a polyethylene cap is then snapped over the top to close and seal the microcell. The internal diameter of the chamber is 2.5 mm and the dimensions of the capped cell are approximately 30 mm diameter by 8 mm high. A sample is measured by placing a filled microcell in a stainless steel holder that is then mounted in the hiRX. Figure 4 depicts a filled microcell in the hiRX sample holder. The chamber and O-ring can be seen through the transparent backing disk. A more detailed description of sample preparation appears later in part B of this section.

As part of the development of the sample handling protocol the optimal filling volume, filling and capping technique, and robustness against leaks and drops were investigated. A volume of 7 μL dispensed while resting the pipette tip on the lip of the sample chamber produces the most reproducible filling. Placement of the microcell cap without direct pressure over the chamber is required. A capping tool was developed to accomplish this task and to reduce the frequency of bubble formation in the sample chamber. The microcells were confirmed to be free of leaks to at least 24 hours and were found to remain closed when dropped from counter height.



Figure 4. Loaded sample microcell with backing disk in place. The sample is colored blue to highlight the chamber. The microcell is resting in the sample holder which will be placed into the hiRX instrument once the microcell cap has been placed on the microcell and the cover has been placed on the sample holder.

Sr calibrations

The hiRX alpha-prototype was calibrated using strontium (Sr) and U solutions while it was installed at LANL. It is possible to use Sr as a nonradioactive surrogate for Pu since the two elements have nearly coincident characteristic X-ray lines (Sr K α 14.164 keV, Pu L α 14.279 keV). Two types of custom calibration were completed including Sr in an aqueous matrix and Sr in a U matrix. While real samples are generally expected to consist of a U-rich matrix, conducting both types of calibration allowed assessment of the impact of the U matrix on the Sr calibration curve. The calibration ranges, particularly for U, were limited relative to the range of samples hiRX is intended to measure. This is because the maximum U content in commercially available aqueous standards is 10000 mg/kg (nominally 10 g/L). The Sr in an aqueous matrix calibration result had correlation coefficient (R^2) of 0.9998 for Sr in eight standards from 0 to 9000 mg/kg (0-9 g/L). The Sr in U matrix results were similar, having an R^2 of 0.9999 for six standards from 0 to 5000 mg/kg (0-5 g/L), while the result for U from 500 to 10000 mg/kg (0.5-10 g/L) was an R^2 of 0.9997. It is evident in Figure 5 by the near overlap of the two Sr calibration lines that the presence of U matrix had little impact on the measured Sr intensities.

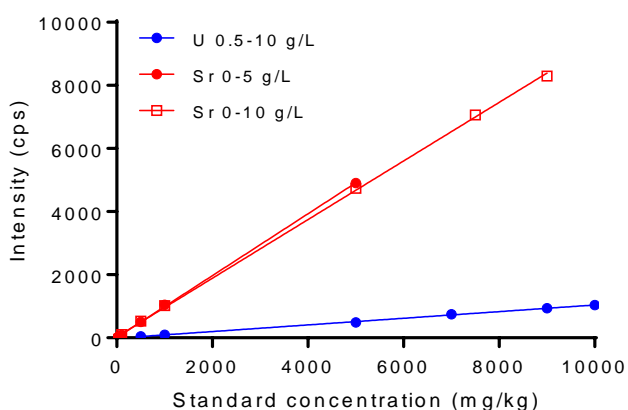


Figure 5. Calibration results for Sr in aqueous matrix (open red square) and Sr (closed red circle) in U matrix (closed blue circle) on hiRX alpha-prototype based on 100 s measurement times and 50 kV, 0.8 mA operating conditions

Accuracy and precision

Initial assessment of accuracy and precision was conducted at LANL using a 1000 mg/kg (1 g/L) Sr solution. The results for eight measurements per day repeated over three days are shown in Figure 6. It should be noted that five sample microcells were used in this assessment, and that

they were carefully rinsed, dried, and reused for each of the three days. While the microcells are intended to be disposable, this approach allowed for the evaluation of repeatability impacted by the instrument operation and microcell filling components. Therefore, potential uncertainty contributions resulting from differences in cell manufacture are not fully represented. Repeatability assessed over multiple days using a new cell on each day is discussed later in this section. Within microcell precision was 0.3 to 0.6% relative standard deviation (RSD), while between microcell precision was 4.9% RSD on days 1 and 2 and 1.3% RSD on day 3. The within microcell results represent instrumental precision, as the microcell was not moved during eight replicate measurements. The maximum bias was -10% for device 5 on day 1, while the majority (11/15) of results had less than $\pm 2\%$ bias. Average bias by microcell ranged from -4 to +2% and average bias by day was -3 to +0.2%.

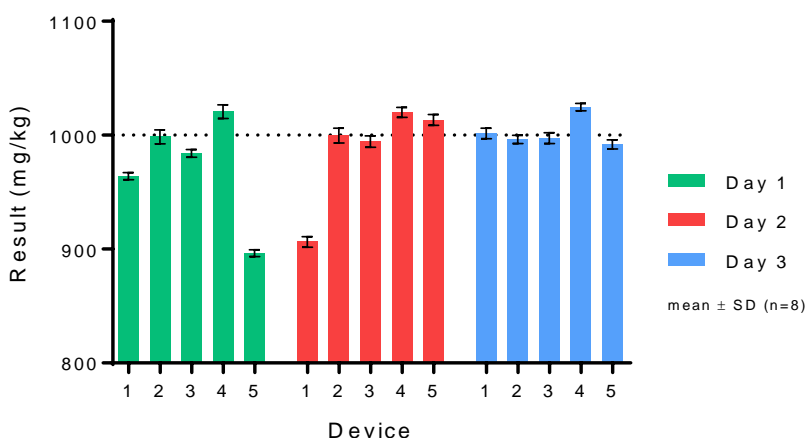


Figure 6. Accuracy and precision of hiRX measurements (100 s) of Sr solution using aqueous matrix calibration; dashed line indicates known standard content of 1000 mg/kg

The limit of detection (LOD) for Sr in an aqueous and in a U-rich matrix was determined based on measurement of a 50 mg/kg Sr solution for 100 s at 50 kV and 0.8 mA (40 W). The LOD for Sr in an aqueous matrix is 0.03 mg/kg (3×10^{-5} g/L) and the LOD for Sr in a 10 g/L U matrix is 0.8 mg/kg (8×10^{-4} g/L). The LOD was calculated as three divided by the sensitivity (net SPP intensity (counts per second (cps)) per unit concentration of analyte) times the square root of the background SPP intensity (cps) divided by counting time (s), as shown in Equation 1 [20].

$$LOD = \frac{3}{m} \times \sqrt{\frac{R_b}{t_b}} \quad (1)$$

This is a typical approach based on counting statistics used to calculate LOD for XRF analytical methods, in which the minimum detectable intensity is assumed to be equivalent to 2σ of the background intensity (95% confidence level).

Pu test analyses

Detection of Pu with the hiRX alpha-prototype instrument was first demonstrated using dried residue of real spent nuclear fuel. The sample was prepared on a typical 32 mm double open ended XRF sample cell and was fixed with polystyrene solution, allowed to dry, and covered with polyimide film. The hiRX spectrum for a residue containing approximately 80 ng Pu is shown in Figure 7 along with a spectrum collected with a conventional commercial micro-XRF instrument, the EDAX Eagle III. Comparing these spectra highlights some of the advantages of hiRX. The hiRX spectrum has only two distinct peaks (U at 13.6 keV and Pu at 14.3 keV) while the

conventional spectrum contains peaks for all of the matrix elements on top of a large bremsstrahlung background, which complicates data interpretation and quantification. An intense U peak from the fuel matrix is present in both spectra, but the Pu peak is barely perceptible in the conventional micro-XRF spectrum. Since the hiRX spectrum has essentially zero background, the peak to background (signal-to-noise) ratio for Pu is 100 times greater for hiRX than for the Eagle III, indicating enhanced sensitivity.

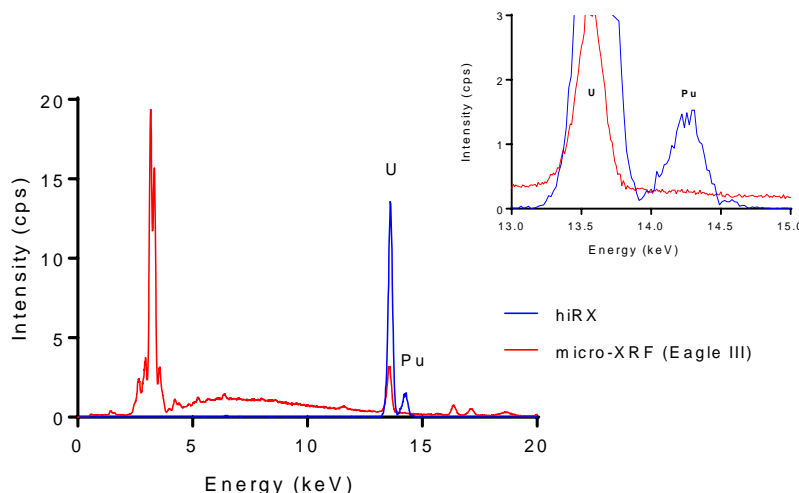


Figure 7. hiRX spectrum (blue, 50 kV and 0.8 mA) and EDAX Eagle III micro-XRF spectrum (red, 40 kV and 0.6 mA) for a portion of a dried residue of spent nuclear fuel containing 80 ng of Pu; inset shows the U/Pu ROI from 13.0 to 15.0 keV

B. Evaluation at Savannah River National Laboratory

The hiRX alpha-prototype was installed for testing at SRNL's nuclear facility laboratory in F-area beginning in July 2014. The primary aims were to calibrate for Pu in aqueous solutions with various U-rich matrices using SRNL-prepared Pu and U reference material solutions, and to measure samples as available from the H-Canyon PUREX and finishing line processes or SRNL laboratory-dissolved Pu oxide product material from HB-Line. Results from these measurements have been evaluated to assess hiRX measurement performance for Pu and U quantification.

Sample handling

An overview of the procedure used for preparing samples in hiRX microcells and then mounting them in the hiRX sample chamber for measurement is shown in Figure 8. It is important to note that no additional sample preparation was required on the front end of the analytical process since any liquid sample can be measured directly with hiRX. Microcells were filled and capped in a radiohood and all parts of the process were conducted in a Contamination Area (CA). These capped microcells were then transferred to another CA lab module and stored in a hood until they could be analyzed on the hiRX instrument. Bulk standard solutions and samples were prepared by an internal standards preparation group before the testing and utilized throughout. Fresh microcells were prepared on each analysis day and measured within four hours. As measurements were completed, microcells were collected in a waste container that will be discarded as a routine-type of radioactive solid waste at the conclusion of the study.



1. Place microcells into tray and slowly dispense 7 μ L into the sample chamber of each microcell using an automatic pipette



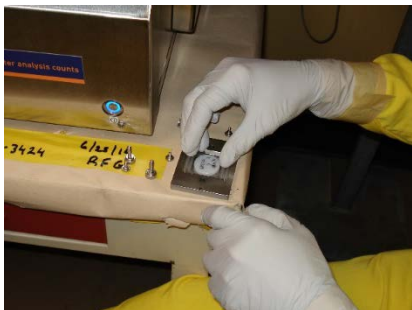
2. Use forceps to place the backing disk over the 7 μ L internal sample chamber within the microcell



3. Use capping tool to close microcells by snapping the cap in position over the backing disk



4. Inspect each microcell for bubbles by viewing the sample chamber within the microcell while illuminated with a flashlight



5. Place microcell in the hiRX sample holder



6. Position sample holder back plate and tighten four thumb screws



7. Mount sample holder in hiRX using two thumb screws and close the interlocking chamber door



8. Enter sample information and initiate measurement using the standalone PC and display

Figure 8. Procedure for filling microcells with sample or standard solution and loading them into the hiRX for measurement at SRNL

Standards preparation

Pu in aqueous matrix standards were prepared from 12U-2 Pu metal from the Plutonium Metal Standards Exchange (PMSE) program. A stock solution was prepared by dissolving a weighed quantity of this metal in nitric acid in order to obtain a final concentration of approximately 10 g/L Pu. This stock solution was then diluted by weight in nitric acid to obtain the Test Sample (TS) concentrations that are listed in Table 1.

Depleted U metal was dissolved in nitric acid to obtain a U stock solution of approximately 400 g /L U. The Pu in U matrix standards were prepared by combining the 10 g /L Pu stock with the 400 g/L U stock solution and diluting with nitric acid by weight to obtain the Calibration (CAL) standard concentrations listed in Table 1.

In both standard preparation methods, a Type A volumetric flask was used on a calibrated analytical balance that was accurate to four decimal places. This allowed for the standard density to be calculated by dividing the measured weight of the solution by the volume of the volumetric flask. This density value was verified by measuring approximately 4 mL of the solution using a densitometer (DMA 4500M, Anton Paar, Ashland, VA).

Reference values for the standards used to calibrate the hiRX are shown in Table 1.

Table 1. Calibration standards for hiRX

Pu Standards in nitric acid (aqueous) matrix	TS Pu 0.1	TS Pu 0.3	TS Pu 0.5	TS Pu 1	TS Pu 3	TS Pu 5
Pu conc. / mg kg ⁻¹	85.9	251.7	483.9	842.4	2548.9	4429.1
Pu conc. ^a / g L ⁻¹	0.102	0.298	0.576	0.995	2.978	5.015
U conc. / mg L ⁻¹ (informational)	0.1	0.3	0.5	0.9	2.7	4.5
Measured solution density / g mL ⁻¹	1.1887	1.1875	1.1908	1.1821	1.1686	1.186
Pu/U Standards in nitric acid (aqueous) matrix	CAL 25-0.1	CAL 50-0.5	CAL 10-1	CAL 5-5	CAL 100-8	CAL 75-10
Pu conc. / mg kg ⁻¹	70.7	414.3	840.9	3066.1	6541.2	8005.3
Pu conc. ^a / g L ⁻¹	0.085	0.512	1.002	3.581	8.001	9.976
Total U (U stock + trace U in Pu stock) / mg kg ⁻¹	20672	40864	8512	4326	81938	59925
U conc. ^a (U stock) / g L ⁻¹	25.06	50.49	10.14	5.05	100.22	74.67
Measured solution density / g mL ⁻¹	1.2123	1.2356	1.1916	1.1681	1.2233	1.2462

^a Concentration calculated from the mass-based Pu concentration (mg/kg) and the solution density (g/mL)

Pu calibrations

The hiRX instrument was calibrated for Pu and U during the spring of 2015 using the standard solutions cited in Table 1, above. The Pu calibration standards contained trace U isotopes from α -decay of Pu isotopes and ^{241}Am from β -decay of ^{241}Pu . The mixed Pu and U standard solutions contained portions of U reference solutions that were added by mass to Pu reference solutions plus the trace U isotopes from α -decay of Pu isotopes and ^{241}Am from β -decay of ^{241}Pu . The hiRX generated a linear regression calibration curve with an R^2 coefficient of 0.9981 for the six Pu standard solutions from 85 to nearly 4500 mg/kg (0.1 to 5 g/L). The hiRX generated a linear regression calibration curve with an R^2 coefficient of 0.9880 for six Pu/U standards solutions with Pu from 70 to 8000 mg/kg (0.08 to 10 g/L) and U ranging from 4300 to approximately 82000 mg/kg

(5 to 100 g/L). The R^2 for U was 0.9778. These R^2 values result from a linear regression fit of the known standard values (y-axis) and the FP result (x-axis). This calculation is performed automatically by the hiRX Solver during the custom calibration (CustCal) process. These calibration plots appear in Figure 9. Since it is convention to plot the independent variable on the x-axis and the instrument response on the y-axis, the known standard values have been plotted on the x-axis and the FP result on the y-axis.

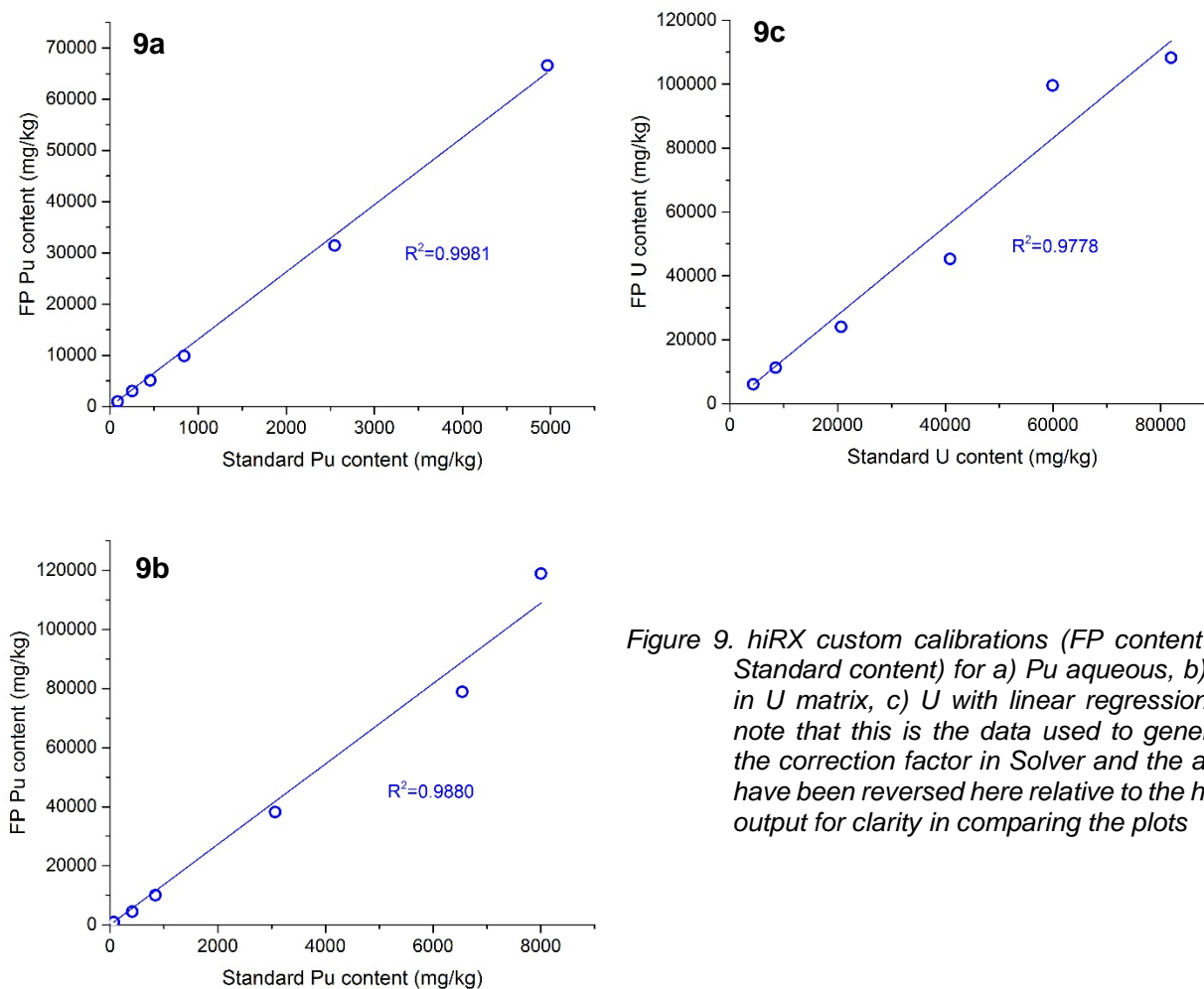


Figure 9. hiRX custom calibrations (FP content vs. Standard content) for a) Pu aqueous, b) Pu in U matrix, c) U with linear regression fit; note that this is the data used to generate the correction factor in Solver and the axes have been reversed here relative to the hiRX output for clarity in comparing the plots

The slope of the custom calibration lines is used as a correction factor to generate the final CustCal result that is reported to the user for hiRX measurements. The CustCal result is calculated in the Solver by multiplying the FP result by the correction factor from the appropriate custom calibration curve. Because the data in Figure 9 have been plotted for clarity with the axes reversed relative to the approach used in the hiRX Solver, the correction factor for these plots would be calculated as $1/\text{slope}$. The slope values used by hiRX Solver for Pu are 0.076 for the Pu in the aqueous solutions and 0.072 for the Pu in the mixed Pu/U aqueous solutions. The slope value is 0.708 for U in the Pu/U aqueous solutions. This somewhat unique approach to calibration was used on hiRX as it is the methodology preferred by XOS in their existing instrumentation. It is intended to first correct the fluorescence intensity data for all X-ray shielding, absorption, and self-absorption effects by the combination of Pu and U in the sample or standard solution using

fundamental parameters. The FP calculations are followed by the application of the conventional instrument calibration process using linear regression curve fitting. Ideally the slope of the Pu custom calibration curves would be independent of the quantity of U in the standards used to generate that curve, however the slope values of 0.076 and 0.072 are 5.4% different from each other, and illustrate that corrections for X-ray shielding, absorption, and self-absorption are not fully addressed by the current FP modeling calculations.

A discrepancy between FP results and known values, for Pu in both aqueous and U-rich matrices, is evident in the custom calibration plots. The FP results are approximately ten times the known content in the standards measured. This is not the case for U where FP results and known values agree within about 20%. The performance for U determination could be considered typical for the FP analysis approach in general while the performance for Pu is unusual. The specific reason for the difference is unknown, but may be traceable to a simple factor-of-10 error within the Solver calculations. Future work will identify and resolve the issue. At present, performing the custom calibrations actually overcorrects for this Pu difference, but brings the CustCal reported results to a more reasonable bias of ~15%. Calibrations for Pu in a U matrix up to 400 g/L will be done at a future time when software and model upgrades have been completed.

Figure 10 shows a different representation of the same custom calibrations. In this case the instrument response plotted on the y-axis is SPP intensity in cps. Though a linear regression fit is shown, it is apparent that the data in 10b and 10c are nonlinear. This is due primarily to matrix effects, particularly self-absorption, which will be discussed in further detail in Section 4. If Figures 9b, c and 10b, c are compared, it is clear that the linear regression is a much better fit for the FP results-based curve than for the intensity-based curve. This indicates that the automatic processing that takes place within the current hiRX Solver does correct to some extent for nonlinearity. While it is not expected that the intensity-based curves be linear, an FP model which fully accounts for matrix effects should produce linear FP results-based curves. Note in Figure 10 the high count rates measured by the hiRX. At approximately 0.8 cps per mg/kg for Pu, 400000 counts for Pu are collected for a 5000 mg/kg standard in only 100 s. This high count rate allows for the rapid acquisition of data for both low and high Pu concentration samples increasing the ability to measure additional repeat samples thereby increasing the statistical accuracy of the hiRX measurements. The much lower count rates for U, about 0.08 cps per mg/kg, are due to the fact that only one DCC segment collects U signal while 3 segments collect the Pu signal.

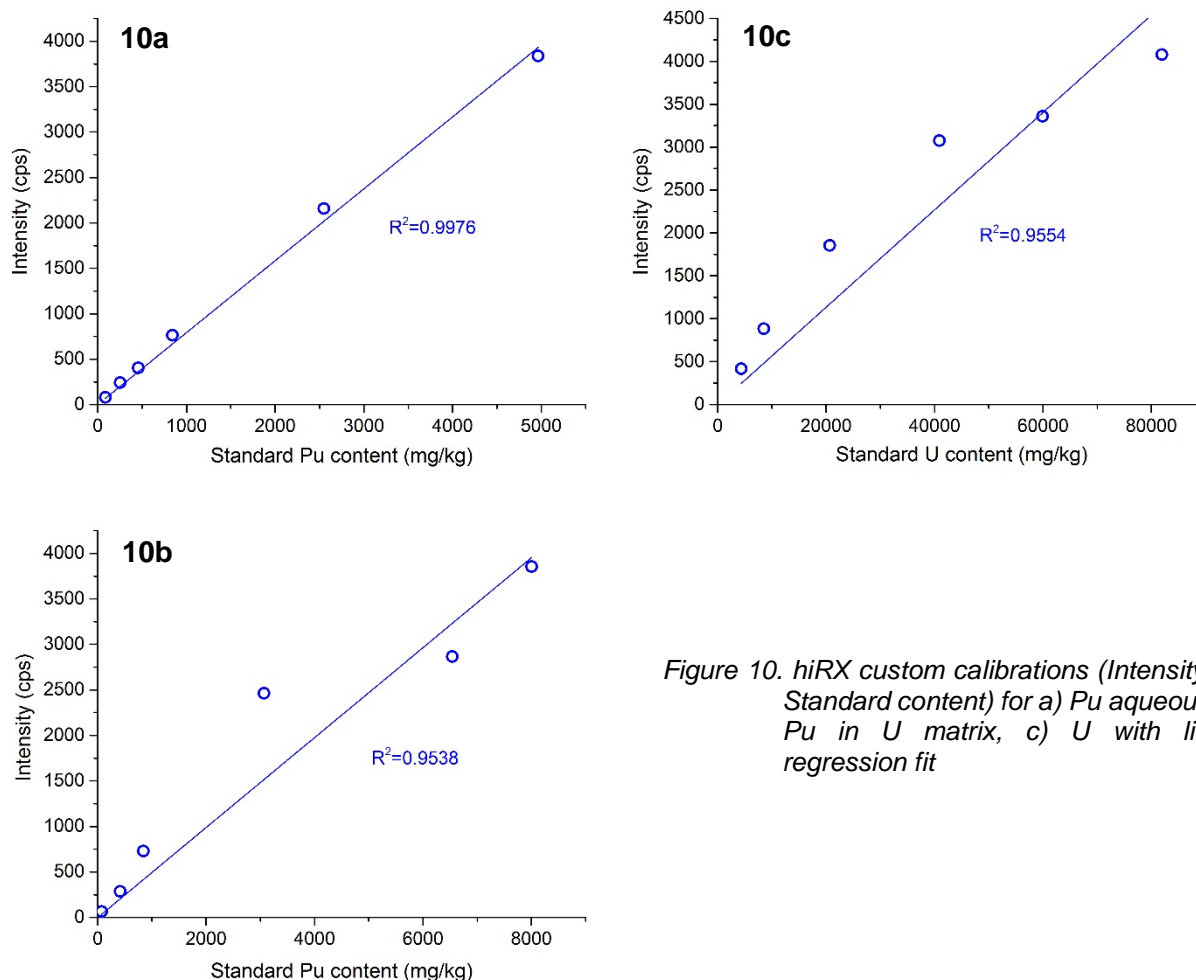


Figure 10. hiRX custom calibrations (Intensity vs. Standard content) for a) Pu aqueous, b) Pu in U matrix, c) U with linear regression fit

Figure 11 shows the same custom calibrations as Figure 9 with the data fitted using nonlinear regression. Since the hiRX GUI currently limits the operator to linear regression, which does not provide the best fit for the data collected, offline processing of the custom calibration data using a second order polynomial was investigated as a means to improve hiRX performance. The results of this effort are covered briefly at the end of Section 3. Using the nonlinear fit the R^2 values improve to 0.9999 for Pu in both aqueous and U-rich matrices and to 0.9989 for U. Working offline, the analyst also has the ability to remove outlying data as has been done for one point on the both the Pu (11b) and U (11c) curves, each of which are identified as red points in Figure 11. The point removed in 11b corresponds to standard CAL 100-8 while the point removed in 11c corresponds to standard CAL 75-10. These data points were removed in order to assess the best-case for sample quantification based on offline processing of the calibration data that was obtained in this study. The points were not removed because there was a recorded issue with the measurement of either of the standards during the calibration or because they were identified as outliers based on a statistical analysis, which are typical justifications to remove a data point. Along with nonlinear fitting, the ability for the operator to review and modify calibrations as appropriate is not a current feature on the hiRX, but this capability should be implemented in the anticipated software upgrade. While improvements to the FP modeling are expected to greatly

reduce or eliminate the need for nonlinear fitting, it should be made available to allow flexibility and address any remaining deviations from linearity.

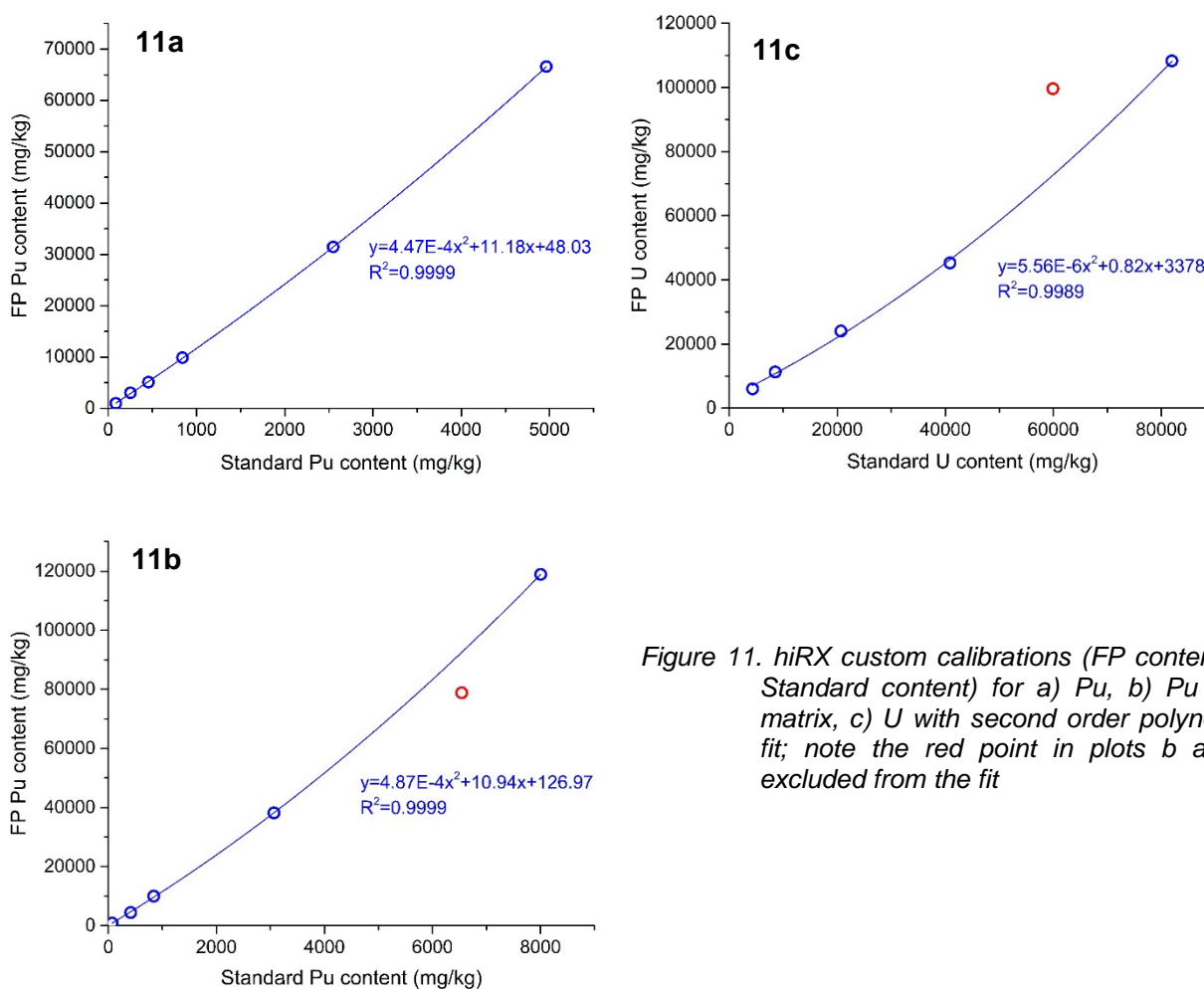


Figure 11. hiRX custom calibrations (FP content vs. Standard content) for a) Pu, b) Pu in U matrix, c) U with second order polynomial fit; note the red point in plots b and c excluded from the fit

Sample descriptions

Three types of real samples were measured on hiRX at SRNL. The first was a plutonium nitrate solution that is being purified in the SRS H-Canyon and will eventually be converted to plutonium oxide product for Alternate Feed Stock #2 (AFS-2) Campaign. This AFS-2 oxide product will be supplied as one of the feed materials for the MOX Fuel Fabrication Facility (MFFF), which is being constructed at SRS. There were four samples of AFS-2 solutions pulled from two H-Canyon tanks: duplicates from Tank 12.1 are referred to here as H777 and H778 and duplicates from Tank 12.2 referred to as H775 and H776. These aqueous samples contained approximately 3 g/L of Pu and trace quantities of U. The second sample was dissolved spent fuel from a Sodium Reactor Experiment (SRE research reactor). Two duplicate composite samples, referred to as SRE 788 and SRE 838 were prepared by combining multiple vials of H-Canyon dissolver solutions. The dissolver samples came from the H-Canyon head-end of the H-Modified Process (a modified PUREX process) and were composed of approximately 4 g/L of U in a nitric acid solution, with trace quantities of Pu. The third sample was a HB-Line Pu oxide product, which was dissolved in a nitric acid solution by the laboratory and is referred to as AFS-2 Can 8. This Pu oxide came

from an HB-Line calcination process and contains approximately 4-5 g/L of dissolved plutonium oxide in a strong nitric acid solution. Table 2 provides a summary of the sample descriptions for quick reference. Question marks in the table indicate that reference values are not available for the given analyte.

Table 2. Description of samples analyzed using hiRX

Type	Sample ID	Concentration / mg/kg ⁻¹		Description
		U	Pu	
AFS-2 (Alternate Feed Stock #2)	H775	2.5	2465.5	Pu nitrate solution, Tank 12.2
	H776	2.8	2488.5	
	H777	2.8	2473.7	Pu nitrate solution, Tank 12.1
	H778	2.9	2470.2	
	Can 8	?	?	dissolved Pu oxide
SRE (Sodium Reactor Experiment)	SRE 778	4391	?	dissolved spent fuel composite
	SRE 838	4391	?	

Results for sample measurements

hiRX performance for quantitation of Pu and U was first assessed by running several of the calibration standards as unknowns. All sample measurements were conducted for 100 s live time. Unless otherwise specified, all results discussed are those calculated directly by the hiRX Solver software based on using one of the two custom calibration curves (CustCal results). Three microcells of TS Pu 0.1 and TS Pu 3 standard solutions were prepared and measured three times each using the aqueous Pu custom calibration curve. Three microcells of CAL 5-5 and CAL 50-0.5 standard solutions were also prepared and measured three times each using the Pu/U custom calibration curve. The results are shown in Table 3. Results for Pu based on both types of calibrations produce a negative bias, ranging from -18 to -6%. Between microcell repeatability which includes instrument and microcell components was <1 to 6% RSD for Pu and up to 8% RSD for U. Within microcell repeatability was 0 to 0.8% RSD and should be considered to represent instrumental precision since microcells were not repositioned between replicate measurements. Two standards were also run over multiple days in order to assess day-to-day variation combined with the impact of using different microcells. One microcell each of the CAL 10-1 and CAL 100-8 standards were prepared and measured six times over the course of five days. These standards served as opening and closing QC checks, as each microcell was run in triplicate at the beginning and end of the analysis day. The between microcell repeatability, which includes instrument, microcell, and analysis day components was 2-3% RSD. Accuracy for Pu quantification over multiple days was similar to the other standards at -15 to -16% average biases. The U bias for standards run as unknowns was generally negative, up to -18%. Figure 12 provides a visual representation of the CAL 10-1 results for each day.

Table 3. Precision and Bias for standards analyzed as unknowns on hiRX

Sample ID	Calibration Used	Standard / mg kg ⁻¹		Mean CustCal Reported / mg kg ⁻¹		RSD		Bias		N
		U	Pu	U	Pu	U	Pu	U	Pu	
CAL 10-1	Pu/U	8512	840.9	7775	718	3.4%	2.9%	-9.3%	-15%	1 cell, 6x, 5 days
CAL 100-8	Pu/U	81938	6541.2	72225	5466	2.4%	2.2%	-12%	-16%	1 cell, 6x, 5 days
CAL 50-0.5	Pu/U	40864	414.3	33409	340	1.4%	1.6%	-18%	-18%	3 cells, 3x, 1 day
CAL 5-5	Pu/U	4326	3066.1	4451	2890	8.3%	6.3%	2.9%	-5.7%	3 cells, 3x, 1 day
TS Pu 0.1	Pu		85.9		73		4.1%		-15%	3 cells, 3x, 1 day
TS Pu 3	Pu		2548.9		2372		0.3%		-6.9%	3 cells, 3x, 1 day

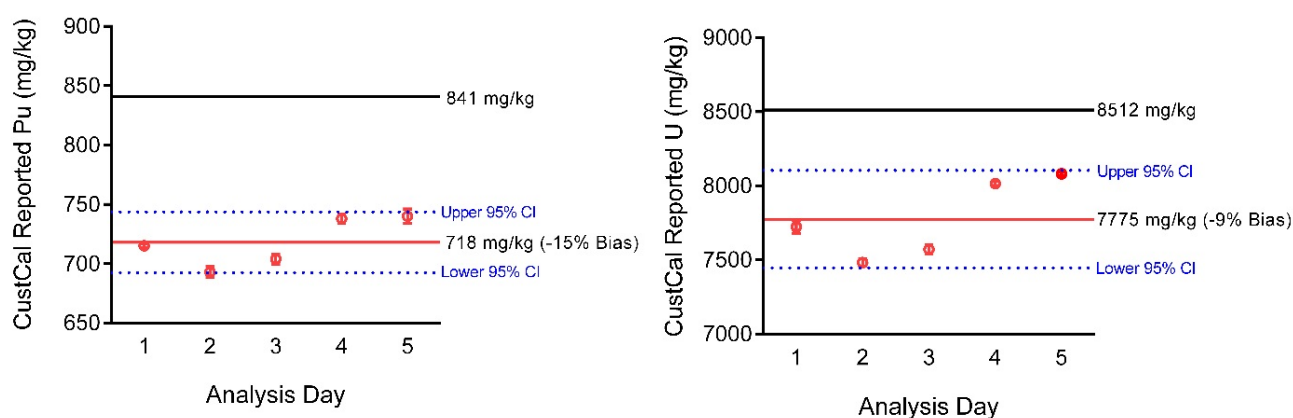


Figure 12. Results for hiRX measurements of CAL 10-1 over 5 days for Pu (left) and U (right) (measured at start and end of day); data plotted are mean \pm SD, $n=6$ for each day; 100 s at 50 kV, 0.7 mA (35 W). Black lines are the known standard values for each sample measured.

The hiRX results for measurement of the real samples described earlier appear in Table 4. The Pu accountability samples (AFS-2) were run using the Pu in aqueous matrix calibration curve since they did not contain U above trace levels (<3 mg/kg). The SRE samples were analyzed using the Pu/U calibration curve to quantify the U concentration. The SRE samples are not expected to contain Pu in any significant quantities, however, no reference analysis is currently available for Pu in these samples. The results for Pu in the accountability samples are more accurate than those for the standards analyzed as unknowns, with average biases between -6 and -2%. Between microcell repeatability was <3% RSD for three of the four samples, and 6% for sample H775. Within microcell precision was 0.2-0.8% RSD. When these results are reviewed graphically in Figure 13, it appears that one of the microcells for sample H775 is an outlier. A possible explanation is that a bubble formed in the chamber of the sample microcell after inspection or was not visible during inspection. Bubbles are discussed in more detail later in Section 4. The same microcells for H775-H778 were also run using the Pu in U matrix calibration for the purpose of comparing performance between the two custom calibrations (data not shown). These results were slightly less accurate with average bias ranging from -10 to -6%. The bias on the U determination in the SRE samples was -24 to -23% with <1% RSD repeatability within and between microcells. When the FP results (which are generated by hiRX without application of a CustCal) are evaluated for these same SRE samples, the means are 4774 mg/kg and 4740

mg/kg, or a bias of 8-9% for U. This illustrates that further evaluation of the modeling is needed, since the CustCal result for standard CAL 5-5 which contained a similar amount of U, in the presence of Pu, was very accurate. While accuracy cannot be assessed for Pu in this sample, hiRX reported approximately 50 mg/kg with <4% RSD between microcells. When these data are considered along with the results for the standard samples, it becomes clear that the CustCal results for Pu in both aqueous and U-rich matrices produce a consistently negative bias, overcorrecting for the significant positive bias that was present in the Pu FP results. This can likely be addressed with changes to modeling of the Solver data processing and the custom calibration approach.

Table 4. Precision and Bias for samples measured with hiRX

Sample ID	Calibration Used	Standard / mg kg ⁻¹		Mean CustCal Reported / mg kg ⁻¹		RSD ^b		Bias	
		U ^a	Pu	U	Pu	U	Pu	U	Pu
H775	Pu		2465.5		2339		6.1%		-5.1%
H776	Pu		2488.5		2343		0.7%		-5.9%
H777	Pu		2473.7		2432		1.8%		-1.7%
H778	Pu		2470.2		2423		2.8%		-1.9%
SRE 788	Pu/U	4391	?	3381	49	0.7%	0.9%	-23%	
SRE 838	Pu/U	4391	?	3357	47	0.8%	3.2%	-24%	

^a Trace U values for H775-H778 excluded from table since the instrument was run in Pu calibration mode

^b N= 3 cells, 3x, 1 day

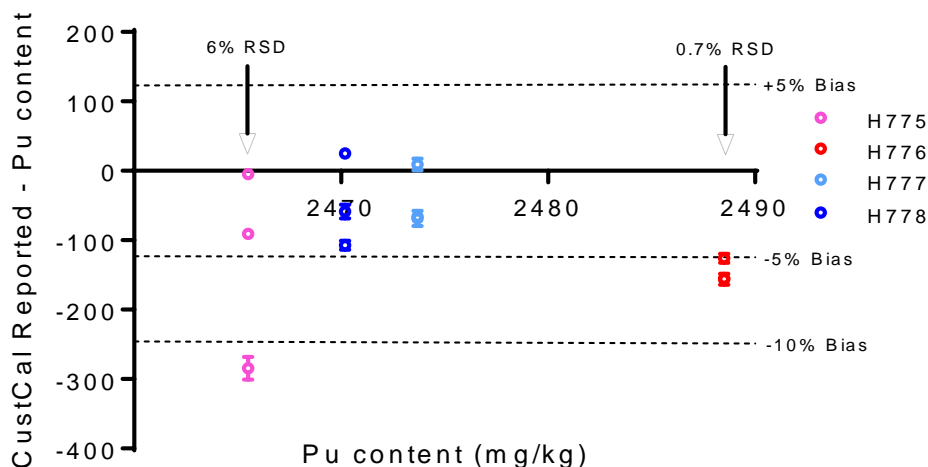


Figure 13. Difference plot (CustCal Reported result – known Pu content vs. known Pu content) for Pu accountability samples; data points are mean \pm SD for 3 cells run 3x per sample (results overlap within H776 and H777)

Three microcells of the AFS-2 Can 8 sample were also prepared and measured in triplicate on hiRX using the Pu in aqueous matrix custom calibration. The mean result was 4476 mg/kg Pu with 1% RSD and 87 mg/kg U with 9% RSD. This material is not expected to contain U; however, the accuracy of the U and Pu determination cannot be assessed since results from a reference analytical technique are not currently available. Spectra from measurement of CAL10-1 and SRE 788 are shown in Figure 14. For CAL 10-1, only the characteristic U L α and Pu L α lines are

present, while for SRE 788 the spectral deconvolution is more complex due to the presence of fission products, possibly Th and Am. We are waiting on confirmation for the presence of these elements in the sample. The LODs for Pu in an aqueous and in a U-rich matrix were calculated based on measurement of TS Pu 1 and CAL 10-1 solutions for 100 s at 50 kV and 0.7 mA (35 W). The LOD for Pu in aqueous matrix is 0.03 mg/kg (3×10^{-5} g/L) and the LOD for Pu in a 10 g/L U matrix is 0.6 mg/kg (6×10^{-4} g/L). Estimated LOD for Pu in a very U-rich matrix, based on use of background counts in the Pu region for a 437 g/L U stock solution is 2 mg/kg (0.002 g/L).

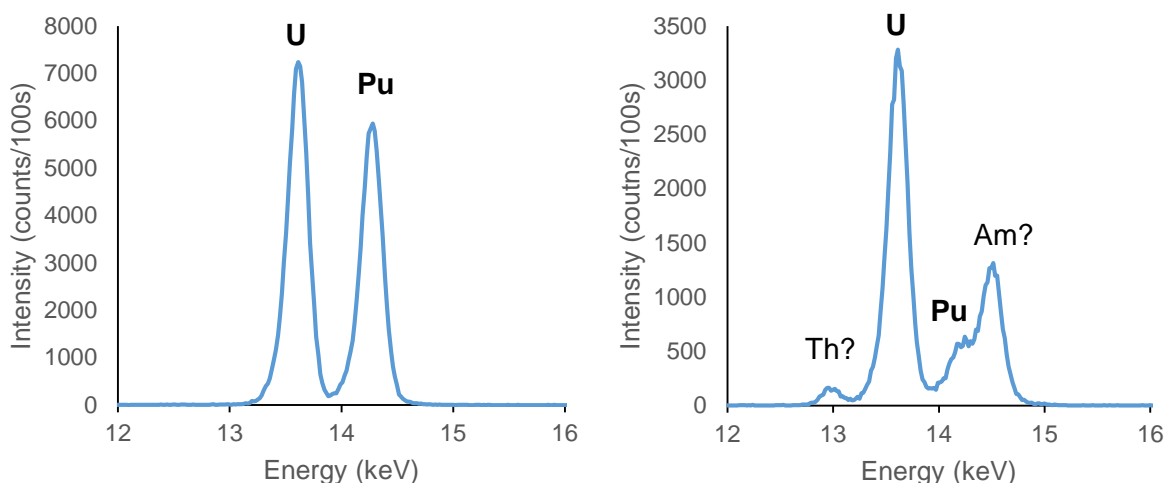


Figure 14. Spectra for CAL 10-1 (left) and SRE 788 (right); 100 s at 50 kV 0.7 mA (35 W)

A spectrum from an SRE sample was also collected with X-ray excitation turned off (Figure 15). The selectivity of the hiRX based on the collection DCC greatly reduces the radiation background outside of the U and Pu bandwidths that would otherwise reach the detector in a conventional micro-XRF system. In the regions of interest for U and Pu, the count rate was <1 count per 100 s.

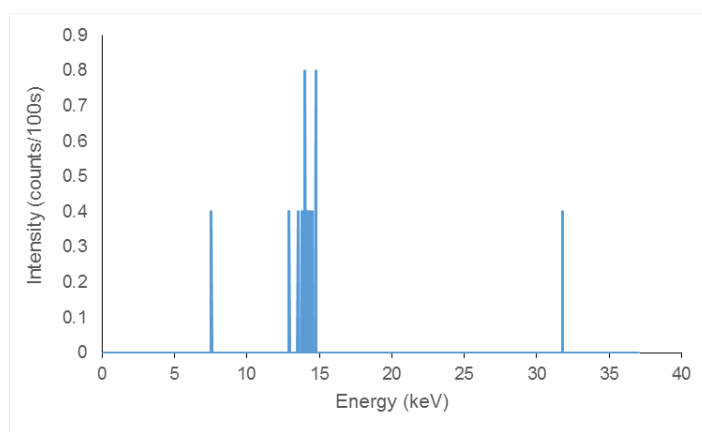


Figure 15. Spectrum for SRE 788; 100 s without X-ray excitation

Offline data processing was evaluated for its potential impact on hiRX results. As previously described, in order to generate CustCal results the hiRX applies a correction factor to FP results based on the selected custom calibration curve, which is fitted using linear regression. In order to generate results for this evaluation, the known correction factors were used to back calculate the FP results, and a quadratic equation based on the CustCal as plotted in Figure 11 was then used to calculate “offline results”. This determination is not independent of the hiRX Solver, since FP-generated results are used, so it does not constitute an assessment of hiRX performance in the absence of its current software. However, it does allow for evaluation as to whether flexibility in calibration and use of nonlinear fitting improves the accuracy of hiRX results. The results are shown in Table 5 and can be compared directly to those in Table 3.

Table 5. Accuracy for standards analyzed as unknowns using offline data processing

Sample ID	Calibration Used	Standard / mg kg ⁻¹		Mean Offline Result / mg kg ⁻¹		Bias	
		U	Pu	U	Pu	U	Pu
CAL 10-1	Pu/U	8512	840.9	8553	858	0.5%	2.0%
CAL 100-8	Pu/U	81938	6541.2	76804	5484	-6.3%	-16%
CAL 50-0.5	Pu/U	40864	414.3	40977	408	0.3%	-1.5%
CAL 5-5	Pu/U	4326	3066.1	3163	3444	-20%	3.2%
TS Pu 0.1	Pu		85.9		82		0.2%
TS Pu 3	Pu		2548.9		2554		-5.0%

For four of the six standards, there was an overall improvement in accuracy based on use of the nonlinear fitting. Results for five of the standards fall below $\pm 5\%$ bias for Pu, while none met this criteria based on the onboard hiRX custom calibration approach. In only one instance, U in CAL 5-5, was there greater uncertainty introduced by the offline calculation. The same process was completed for the real samples (data not shown). The results for the AFS-2 samples based on the Pu in aqueous matrix calibration remained essentially unchanged with bias of +2 to +6% while results for the same samples based on the Pu in U matrix calibration improved to a bias of +1 to +5%. This approach was not found to be a benefit to the SRE samples, with biases on the order of -60%. These results should be considered preliminary, as additional offline processing of the existing data will be conducted in the near future. However, this indicates that with modification to the data processing functions, in particular the fundamental parameters calculations and the custom calibration methodology installed in the hiRX Solver, the accuracy of future measurements could be improved significantly and the ease of instrument operation and functionality maintained.

Section 4. Identified limitations and prescriptions for improvement

Bubbles

The inclusion or formation of bubbles was identified over the course of the hiRX evaluation as a limitation of the current sample microcells. Bubbles affect the accuracy and precision of measurements by reducing the sample mass and thus analyte signal collected from the interrogated volume producing an erroneously low result for Pu content in the sample. The impact of bubbles on hiRX quantitation was tested by measuring Pu accountability sample microcells known to contain bubbles of varying size, classed as large or small. Bubbles that appeared to fill most of the chamber were classed as large, while bubbles thought to occupy less than a quarter of the chamber volume were considered to be small. Small bubbles typically occur at the edge of the chamber. The results are shown in Figure 16 along with a photo of a large bubble. A significant decrease in reported Pu content of 60 to 90% occurred for large bubbles relative to the mean

results for sample microcells not containing bubbles. For the small bubble identified in a microcell of sample H776, a reduction of 15% in reported Pu occurred. Because the microcells were not repositioned between replicate measurements, there was little difference in precision for samples with bubbles at <1% RSD compared to those without. Note that the error bars for the NB (no bubble) samples in the figure represent between microcell repeatability while those for LB (large bubble) and SB (small bubble) indicate within microcell repeatability, so they cannot be compared directly.

The step in the sample preparation found to be most likely to introduce a bubble is the capping procedure, while pipetting the sample is somewhat less likely to result in the inadvertent inclusion a bubble. Once these were identified as areas of concern, controls were put into place to limit the impact of bubbles on the hiRX measurements at SRNL. These included an increase in sample volume from 5 to 7 μL to reduce the headspace in the analytical chamber, use of a capping tool to eliminate direct pressure over the sample chamber while closing the microcells, and viewing prepared microcells with backside lighting to identify and discard any microcells containing bubbles. These efforts have been successful in managing bubble issues, with only a small number of results identified as likely to have resulted from a microcell containing a bubble. Redesign of the sample microcell or transition to a fixed-geometry flow cell is being considered to further improve hiRX performance and ease of operation. This would require some hardware modifications to the current design of the hiRX sample chamber and door to accommodate the flow cell and input and output lines, while maintaining appropriate shielding and interlock features for the operation of the X-ray source.

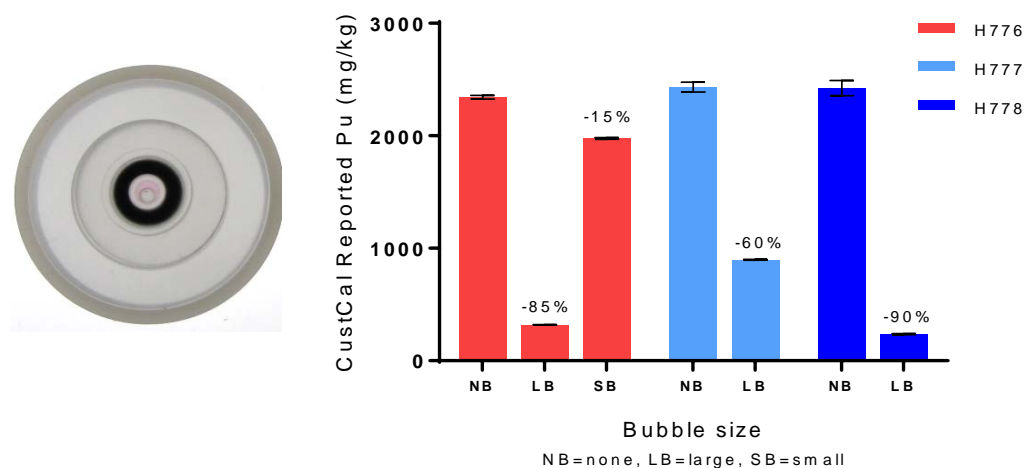


Figure 16. Image of a large bubble in a colored H_2O solution viewed from the analysis side (left); Results for accountancy sample cells known to contain bubbles, NB is the result mean \pm SD, $n=9$ for all measurements without bubbles, while LB and SB are mean \pm SD, $n=3$ for a single cell containing a bubble (right).

Modeling and data handling

Absorption matrix effects have an impact on the Pu and U results as presently generated by hiRX. This is particularly evident in the nonlinear trend in the calibration of U up to 100 g/L, but also to a lesser extent for the calibration of Pu in a U matrix up to 10 g/L. While the results are not shown in this report, an initial calibration with a U matrix up to 400 g/L was found to be very nonlinear for U, with a significant decrease in the response of the system versus changes in standard concentration observed between 100 and 200 g/L. Subsequent calibration of the instrument was limited to 100 g/L U to minimize the impact of potential nonlinearity, with some success.

A description of all of the matrix effects impacting the U and Pu calibrations is beyond the scope of this report, but a basic explanation may be useful to the reader. As U content in the matrix increases, both the penetration depth of exciting X-rays and the escape depth of characteristic X-rays are reduced, impacting U signal intensity. These matrix absorption effects also have an effect upon Pu intensity, but, the greater impact on Pu determination in a U-rich matrix is due to the appreciable U background in the region of the Pu peak which must be included in the model. A hardware improvement that would enhance hiRX performance with regard to the matrix effects is the addition of a channel (DCC optic) to collect Compton scatter at approximately 19 keV. With addition of this segment to the 360 degree revolved optic the signal for Pu, U, and Compton scatter would be collected simultaneously. The intensity of Compton scatter is proportional to the mass density of the sample, so measured Compton intensity can be used to empirically correct results for the extent of absorption occurring in each sample. This would also be useful in identifying any microcells with bubbles present.

Suggested Upgrades

Several upgrades to data handling and software have also been identified to improve upon the present performance. It is anticipated that even in the absence of any hardware upgrades, this effort will improve hiRX accuracy and reduce uncertainty in the current alpha-prototype. First, refinement to the U model is required. We propose to accomplish this by preparing and measuring with the hiRX a small number of additional samples at SRNL, which will help XOS to improve the spectral deconvolution and the FP model for Pu in U matrices and for U itself. The samples will contain varying U content from 10 to 400 g/L with constant 1 g/L Pu and fission products. At the completion of this measurement effort, it should be possible to reprocess the data already obtained during the field testing to assess the extent of improvement (though the existing custom calibrations would still have to be relied upon for this type of evaluation). An additional set of test samples containing Pu and U at approximately 1:100 g/L Pu:U levels with fission products were not available during the field testing, and should also be prepared and measured to evaluate upgraded hiRX performance for the target sample type. Second, modification to the GUI and Solver for “smart” processing of data is suggested. The concept is that additional input by the operator on the front end, via a dropdown type menu where the type of sample or matrix can be selected based on knowledge of process, when available, will improve the accuracy of hiRX results. The functionality behind this is that the Solver will not attempt to automatically perform deconvolution and fit characteristic peaks for U, Pu, or fission products that are not present in the sample, as is currently the case. Further suggested upgrades to the GUI include more flexibility in calibration (e.g., the ability to remove a point or use nonlinear fitting) and enhanced access to raw data for instrument development and software refinement. The ultimate goal would be development of a “smart” Solver model to correctly assess the sample composition from the collected spectrum, and in concert with the knowledge of process entered, apply the appropriate background and element corrections to give a highly accurate and precise analysis of the Pu and U content of the sample.

The following data should be collected at SRNL to improve the spectral deconvolution and the FP model:

- U solutions at 10, 25, 50, 75, 100, 200, 300, and 400 g/L spiked with 1 g/L Pu and fission products; prepare each solution in two microcells and measure 3x each
- Well characterized real spent fuel containing fission products, or lab-prepared surrogate, containing both Pu at 1-2 g/L levels and U at 100 g/L level; prepare solution in three microcells and measure 3x, repeat 5 days

Potential Applications at SRNL (SRS)

The Analytical Laboratories in F-Area provides a variety of measurement services in support of SRS nuclear material processing, material stabilization, and waste handling missions including plutonium and uranium measurements for process control, material control and accountability, material characterization, waste characterization, and product specification. The hiRX instrument has the potential to satisfy the data quality objectives in several areas assuming that enhancements to the software and hardware are completed effectively:

- The hiRX instrument is capable for direct measurement of sample solutions without sample pretreatment combined with low instrument detection limits for both Pu and U. Accountability and process control measurements on low concentration plutonium and uranium process and waste streams in the H-Canyon, HB-Line, H-Area Outside Facilities, and the SRS Waste Tanks normally require extensive sample handling and pretreatment to achieve 10-20% measurement uncertainties using kinetic phosphorescence analysis for uranium and alpha spectroscopy for plutonium. The hiRX is capable of rapidly determining both uranium and plutonium from the same sample aliquot, without sample preparation or purification. It is also capable of providing Pu and U verification measurements on the purified solutions that are measured for U by KPA and Pu by Alpha Spectrometry.
- In most cases where kinetic phosphorescence analysis is applied for uranium measurement, the hiRX instrument could be calibrated to provide a more rapid uranium measurement with at least comparable reliability. Completing the anticipated/proposed improvements to the hiRX spectral modeling and calculations would ensure that improvement in efficiency, turnaround time, and measurement reliability would be achieved.
- The hiRX should be effective for some of the accountability and process control Pu measurements that support AFS-2 process in H-Canyon.
- The hiRX should also be effective for most of the accountability and process control Pu measurements that support AFS-2 process in the HB-Line Nuclear Facility in preparation for plutonium oxide powder production for the MFFF.
- The hiRX concentration measurements could be a more rapid method for pre-screening Pu and U measurements that are performed before each isotope dilution mass spectrometry measurement performed using the thermal ionization mass spectrometer.
- The HB-Line Nuclear Facility dissolves and discards non-MOX-able plutonium and mixed Pu/U scrap materials to the H-Canyon for eventual transfer to the SRS high-level waste tanks. The hiRX Pu and U concentration measurements should be applicable to some of the sample points associated with this processing.
- Measurement of U and Pu for process control and accountability for Spent/Used Nuclear Fuel processing in the H-Canyon should also be a target area for the hiRX technology. Both process control and accountability sample points for Pu and U concentration are applicable.
- The hiRX technology would need to be enhanced as proposed in this report, but if completed successfully, the instrument would likely compete favorably with absorption spectroscopy technology, which the SRNL Analytical Laboratories apply for some key Pu and U accountability measurements in H-Canyon and HB-Line.

Even in its current state as a prototype instrument with known deficiencies the hiRX instrument is still capable of providing complementary analytical capabilities in each of the areas listed above, although the scope would need to be tailored appropriately.

Impact of initial update to the FP model: reprocessed results

The results of the hiRX evaluation at SRNL clearly indicated that refinement of the FP model is required. Recall that FP-based results, which are automatically generated by hiRX Solver, were approximately ten times higher than expected for Pu and up to 20% elevated for U (see Figure 9). The custom calibration process applied a CustCal correction factor to the FP results, producing the CustCal results that have been detailed in this report. The CustCal results exhibited a consistently negative bias, due to overcorrection occurring in the Solver. While the custom calibration process is intended to enhance accuracy by adjusting small biases in FP results that may be due to issues such as nonlinearity, it is not suited to correct for the type of gross error observed for Pu using the FP model during the testing.

Following the completion of the testing at SRNL, the FP model was re-evaluated by XOS using a subset of the data collected. Geometric constant values for both Pu and U were modified and results for all measurements were recalculated based on the FP model which contains the updated constants. The revised data appear in Table 6. The results can be compared to those in Tables 3 and 4, where CustCal results were reported, and Table 5, where Offline results are shown.

Table 6. Accuracy for standards analyzed as unknowns and samples using updated FP model

Sample ID	Standard / mg kg ⁻¹		Mean Updated FP Result / mg kg ⁻¹		RSD		Bias	
	U	Pu	U	Pu	U	Pu	U	Pu
CAL 10-1	8512	840.9	9160	863	3.3%	2.8%	7.6%	2.7%
CAL 100-8	81938	6541.2	56588	4454	1.3%	1.1%	-31%	-32%
CAL 50-0.5	40864	414.3	39316	408	1.3%	1.5%	-3.8%	-1.6%
CAL 5-5	4326	3066.1	4603	3057	7.0%	5.2%	6.4%	-0.3%
TS Pu 0.1		85.9		88		4.1%		2.5%
TS Pu 3		2548.9		2503		0.3%		-1.8%
H775		2465.5		2471		5.3%		0.2%
H776		2488.5		2475		0.6%		-0.5%
H777		2473.7		2557		1.6%		3.4%
H778		2470.2		2549		2.4%		3.2%
SRE 788	4391	?	4178	61	0.8%	1.4%	-4.9%	
SRE 838	4391	?	4151	60	0.8%	3.2%	-5.5%	

Selecting an example is perhaps the best way to highlight the impact of the updated FP model on the data. The known standard value for Pu in CAL 10-1 is 840.9 mg/kg. The mean FP result based on the original model was 9917 mg/kg (>+1000% bias), while the mean CustCal result was 718 mg/kg (-15% bias). The mean Offline calculated result was 858 mg/kg (+2% bias) while the mean FP result based on the modified model is similar at 863 mg/kg (+3% bias). Table 7 highlights this considerable improvement in hiRX performance for accuracy in Pu and U results indicating the biases on each of the result types discussed in this report. Additional modifications to the modeling and data handling, such as improved spectral deconvolution, are still required. The improvement in hiRX FP results between the original model and the updated model is significant, especially for Pu, where mean FP results now agree to within $\pm 5\%$ of the known value for five of six standards and all real samples measured. For the majority of the standards and samples, the updated FP results were even more accurate than the Offline results. In only one instance, for Pu and U in

CAL 100-8, was there greater uncertainty introduced by the updated FP result (the results for CAL 100-8 indicate something may be wrong with this measurement or sample i.e., undetected bubble). Updated CustCal results cannot be effectively calculated without performing new calibrations, since they are specific to the reported FP content, but, the application of new custom calibrations is expected to further improve hiRX accuracy to be consistently in the <1-5% range. The reprocessed measurement data demonstrates the analytical capability of the hiRX prototype for accurate Pu and U analyses of spent nuclear fuel.

Table 7. Accuracy for all result types

Sample ID	Standard / mg kg ⁻¹		Bias FP Result		Bias CustCal Reported		Bias Offline Result		Bias Updated FP Result	
	U	Pu	U	Pu	U	Pu	U	Pu	U	Pu
CAL 10-1	8512	840.9	29%	1075%	-9.3%	-15%	0.5%	2.0%	7.6%	2.7%
CAL 100-8	81938	6541.2	24%	1049%	-12%	-16%	-6.3%	-16%	-31%	-32%
CAL 50-0.5	40864	414.3	15%	1027%	-18%	-18%	0.3%	-1.5%	-3.8%	-1.6%
CAL 5-5	4326	3066.1	45%	1196%	2.9%	-5.7%	-20%	3.2%	6.4%	-0.3%
TS Pu 0.1		85.9		1021%		-15%		0.2%		2.5%
TS Pu 3		2548.9		1124%		-6.9%		-5.0%		-1.8%
H775		2465.5		1148%		-5.1%		2.2%		0.2%
H776		2488.5		1139%		-5.9%		1.5%		-0.5%
H777		2473.7		1193%		-1.7%		5.6%		3.4%
H778		2470.2		1191%		-1.9%		5.4%		3.2%
SRE 788	4391	?	8.7%		-23%		-62%		-4.9%	
SRE 838	4391	?	7.9%		-24%		-63%		-5.5%	

Summary/interpretation on hybrid calibration approach

In addition to the above assessment on the impact of the update to the XOS FP model on hiRX accuracy, an independent analysis of hiRX calibration was conducted by Patrick O'Rourke of SRNL. *hiRX Hybrid XRF Calibration*²¹ describes an offline calibration method which combines an FP approach with the peak-ratio method to correct for X-ray self-absorption. Control of microcell fill and sample thickness, X-ray intensity, and dead-time corrected count time were highlighted as critical for accurate prediction of concentration, while solution density input was of lesser impact. Using this approach, errors in predicted results for Pu and U in calibration standards treated as unknowns were generally <±0.3%. This result supports the need for careful reevaluation and refinement of the FP model and particularly the linear calibration approach currently implemented on the hiRX alpha-prototype.

Summary/interpretation of uncertainty evaluation

In order to better understand and to quantify the sources of measurement uncertainty for the alpha-prototype hiRX instrument, a *Guide to the expression of uncertainty in measurement*²² (GUM)-compliant analysis was conducted based on the results of the performance testing at SRNL. The report *GUM-compliant uncertainty propagations for Pu and U concentration measurements using the alpha-prototype XOS/LANL hiRX instrument; an SRNL H-Canyon Test Bed performance evaluation project*²³ utilized the information from this report and from the *hiRX Hybrid XRF Calibration* report to perform the analysis. The major findings of the GUM analysis are summarized in context below, with some content extracted directly from the report.

As it is currently configured and operated, the hiRX alpha-prototype produces measurement results that have an expanded uncertainty of 10% ($K=2$ coverage factor, 95% confidence interval) for Pu within the optimum concentration range of 1-20 g/L total Pu and U (sum of analytes). For various mixtures ranging from 0.1-10 g/L of each analyte, relative expanded uncertainties range from 9.6-10% for Pu and 9.5-16% for U. For higher total Pu and U content (up to 250 g/L), relative expanded uncertainties are 9.5-23%.

The preparation of samples, in particular use of the disposable microcell, was identified as the largest single component of the expanded uncertainty of hiRX measurements. In contrast, while the machining of the designed 1.00 mm analytical chamber depth was found to be both accurate and precise when empty microcells were measured with a calibrated depth gauge (1.00 ± 0.01 mm, $K=1$), the effective thickness, which was assessed based upon hiRX spectra of filled cells, exhibited variability on the order of 5% ($\sim 1.227 \pm 0.056$, $K=1$). A possible explanation for the apparent increase in cell thickness is that the o-ring installed within the microcell to ensure an effective seal of the sample chamber presses the backing disk away from the chamber and towards the snap cap, physically increasing the available volume. This theory is supported by the finding that the 5 μ L of sample which should have filled the chamber as designed was not sufficient to prevent the routine generation of bubbles due to capture of air, prompting the use of 7 μ L of sample during the evaluation at SRNL. The variation in effective thickness between microcells impacts the FP shielding calculations, and thus the reported Pu and U results, by approximately 3.5%. The formation of bubbles in the microcells, which was identified during the hiRX evaluation as a limitation of the current sample microcell, was considered a negligible potential source of uncertainty relative to the uncertainty in the variables that impact the shielding calculations, in part because the inspection for bubbles prior to measurement increases the reliability of microcell use. The additional potential sources of uncertainty involved in introducing a sample solution using a microcell include variation in solution handling and loading into microcells and the consistency of aligning the microcell within the sample mount and in the hiRX instrument. Separate terms for other aspects of sample preparation including sample collection and subsampling were not included in the uncertainty propagation.

The determination that the positioning and thickness of the sample chamber are the input variables with the largest variance contribution to hiRX measurements agrees with operator observations during the field testing as well as prediction by technical staff. It was recognized that a flowcell or in-line arrangement would likely reduce uncertainty, but considerations such as the need to operate such a system within radiological containment at SRNL and associated costs were weighed against the desire to work on a benchtop and to return the instrument to LANL at the conclusion of the evaluation. For the microcell thickness currently being used, the FP model appears to be effective for samples containing total actinide concentration up to 100 g/L. Modifying the thickness of the microcell would be an easy approach to shift the optimum range for hiRX measurements, but would not address variability in effective thickness. Thus, the principal recommendation for enhancing hiRX performance is a fixed-geometry sample chamber, incorporating flowcell technology. Further, design of syringes (no headspace containers) of small capacity to be used for sample addition directly to a flowcell mounted in the hiRX instrument or into microcells if desired, is suggested.

Several recommendations for refinement and development of data handling in the hiRX beta-prototype were identified to reduce instrument-driven uncertainty, including:

- Inclusion of contributions of other high-Z elements such as Th, Np, and Am when known to be present as well as elements that may be present in significant quantities from cladding materials such as Al and Zr in FP modeling;

- Improved detection and handling of interferences, such as spectral correction to the Pu measurement with reliability consistent with the confidence to which Sr concentration is known and no correction when Sr is not present;
- Consideration that the standard linear regression used in the CustCal is not properly weighted and that the larger the correction for shielding the greater the uncertainty in the resulting slope and sensitivity terms.

The latter is particularly important as the CustCal values are expected to be 30-50% of the variance budget depending on the calibration range and the number of measurements used to generate the curve. Recommendations for internal hardware which have the potential to reduce uncertainty in hiRX measurements included:

- Refocusing of DCC crystal segments so that Pu and U signals are focused on different SDDs to reduce the spectral overlap of the Pu and U peaks;
- Addition of a detector to monitor X-ray intensity from the tube to allow normalization of results to average intensity of standard and sample measurements.

The GUM model equations were also used to evaluate the potential improvement in performance for a hiRX beta-prototype instrument which incorporates the above suggested modifications to hardware and software, including a flow cell in fixed geometry. For total Pu and U at 1-20 g/L, predicted relative expanded uncertainties of 0.76-1.1% for Pu and 0.86-4.1% for U should be achievable. A performance improvement that exceeds these estimates may be possible. The prediction places hiRX performance within the 2.8% international target value (ITV) for XRF assay of low concentration Pu solutions²⁴ and approaches the <1% ITVs for various materials using destructive analysis methods.

Section 5. Conclusion

The overall performance of hiRX in both the calibration of Pu in aqueous and U matrices and the measurement of Pu and U in real samples is good considering this is an alpha-prototype which includes both new hardware and software. The testing at SRNL was successful since the data collected were informative and valuable providing some insight as to the sources of error in the measurements. Achieving the target bias of less than 1% is feasible and some of the results demonstrated potential for meeting this target. Independent analysis of the test data using both an offline calibration methodology and a GUM analysis validates the hiRX performance. These efforts identified sources of bias which if corrected would improve the hiRX performance to be within the target ITVs of less than 1%.

Testing of the hiRX alpha-prototype at SRNL involved calibration using standards that covered both aqueous Pu and Pu spiked U matrix solutions. The initial calibration and measurements of real samples indicated some negative bias which was attributed to incorrect FP model parameter settings. Reprocessing the hiRX data with an updated FP model *significantly* improved results with sample biases of -5% for U and -0.5 to +3% for Pu. The initial calibrations gave R^2 values for linear fits of the measured Pu standards of 0.9981 for the aqueous calibration and 0.9880 for the Pu in U matrix. The U calibration R^2 value was 0.9778. Further refinements of the modeling software are expected to significantly reduce uncertainty of the Pu and U measurements. These results clearly demonstrate the potential of hiRX for Pu measurements in safeguard applications as well as general purpose actinide element measurements in a variety of processing applications. Hardware upgrades will aid in empirically correcting U matrix effects on both the Pu and U quantification. The demonstrated simplicity of the hiRX measurement process has highlighted potential applications within Savannah River Site. The ability to rapidly prepare samples with no sample pretreatment, using a 7 microliter sample volume, which reduces the handling hazards and waste disposal issues, makes the hiRX an attractive instrument for Pu and

U analyses in spent nuclear fuel samples, for MC&A, and waste profile characterization to name some potential applications.

Section 6. Report Glossary and Abbreviations

Glossary

Custom calibration (CustCal)

The process of calibrating hiRX. Also refers to results generated by the hiRX based on use of user generated calibration curves. The custom calibration applies a correction factor to FP results.

Doubly curved crystal (DCC)

Toroidally bent crystal monochromator

Fundamental Parameters (FP)

Refers to results generated by the hiRX without use of a custom calibration. The fundamental parameters approach to quantitation is based on the use of known physical constants and experimental parameters, without calibration by the user.

Graphical user interface (GUI)

Interface where the user interacts with hiRX to input parameters, direct the measurement of samples, and view results.

High Resolution X-Ray (hiRX)

Instrument based on monochromatic WDXRF for sensitive and selective measurement of Pu and U in spent fuel matrices. High resolution refers to the specificity provided by the collection DCC – only Pu and U peaks are present in the spectrum.

Spectrum Pre-Processor (SPP) intensity

Net counts for the element of interest arrived at by summing the counts for the major line after background subtraction and peak deconvolution.

Wavelength dispersive X-ray fluorescence (WDXRF)

A type of XRF in which specific wavelengths (energies) of characteristic X-ray radiation are separated with an analyzer crystal and measured either sequentially or simultaneously.

Abbreviations

AFS-2	Alternate Feed Stock #2
ALARA	As Low As Reasonably Achievable
cps	counts per second
GUM	Guide to the expression of uncertainty in measurement
HKED	Hybrid K-edge Densitometry
IDMS	Isotope Dilution Mass Spectrometry
KPA	Kinetic Phosphorescence Analysis
LANL	Los Alamos National Laboratory

LOD	Limit of Detection
MC&A	Materials Control and Accountability
MFFF	MOX (Mixed Oxide) Fuel Fabrication Facility
PMSE	Plutonium Metal Standards Exchange
ppm	parts per million (by weight; mg/kg)
PUREX	Plutonium Uranium Redox Extraction
RSD	Relative Standard Deviation
SRE	Sodium Reactor Experiment
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TEVA	Tetravalent Actinides
TIMS	Thermal Ionization Mass Spectrometry
XOS	X-Ray Optical Systems, Inc.

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